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## Report Title

### ABSTRACT

This three-year research program studied wholly aromatic, optionally fluorinated copolymers with the goal of establishing fundamental data about the complex relationships between PEM chemical structure, morphology, transport properties, and the performance of the DMFC fuel cell membranes. Accomplishments included the generation of lower permeability, high-power density PEM systems. Under ARO funding, we were also successful in scaling the ion containing comonomer in a single step (at the kilogram quantity or higher) as well as demonstrating viable routes for the synthesis of the desired copolymers. This funding also contributed to developing materials for the electrode catalyst layers that show competitive advantages over Nafion. MEAs were prepared, which were characterized by voltage current curves (primarily at LANL) and 300 hours stability at 80 degrees C was demonstrated.

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**List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

D.B. Baird, H.Huang, and J.E. McGrath, "Polymer Electrolyte Membrane Fuel Cells," *Plastics Engineering*, 59(12), 46-55, (2003).

Y.S. Kim, F. Wang, M. Hickner, T.A. Zawodzinski, and J.E. McGrath, "Fabrication and Characterization of Heteropolyacid (H3PW12O40)/Directly Polymerized Sulfonated Poly(arylene ether sulfone) Copolymer Composite Membranes for Higher Temperature Fuel Cell Applications," *Journal of Membrane Science*, 121 (1-2), 263-282 (2003).

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**(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)**

K.B. Wiles, V. A. Bhanu, F. Wang, M.A Hickner, and J.E. McGrath. Poly(arylene thioether sulfone) Copolymers for PEM-Based Fuel Cell Systems, Polymer Preprints 2003, 44(1), 1089.

Harrison, William L.; Wang, Feng; O'Connor, Kerry; Arnett, Natalie Y.; Kim, Yu Seung; McGrath, J. E. Sulfonated poly(arylene ether sulfones) containing hexafluoroisopropylidene unit: Influence of sulfonic acid position on stability and other properties. Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (2003), 44(1), 849.

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M.L. Hill, B.R. Einsla, Y.S. Kim, and J.E. McGrath. Synthesis and Characterization of Sulfonated Poly(arylene ether sulfone)/Zirconium Phenylphosphonate Composite Membranes for Proton Exchange Membrane Fuel Cell Applications, American Chemical Society, Division of Fuel Chemistry Preprints, (2004), 49(2), 584-585.

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B.J. Akle, D.L. Leo, J.L. Hickner, and J.E. McGrath. Electroactive Polymers Based on Novel Ionomers: Proceedings of the ASME Aerospace Division, 2003, 455-452.

Number of Papers published in non peer-reviewed journals: 17.00

(c) Papers presented at meetings, but not published in conference proceedings (N/A for none)

North American Membrane Society Meeting, June, 2004, Honolulu, Hawaii.  
Gordon Confernece on Membranes, July 2004, New London, Connecticut.  
Advances in Polycondensation 2004, September 2004, Roanoke, VA.

Number of Papers not Published: 3.00

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

Melinda Hill, 1.0 (2 years)  
Michael Hickner, 1.0 (1 year)

Number of Graduate Students supported: 2.00

Total number of FTE graduate students: 3.00

Names of Post Doctorates

Number of Post Docs supported: 0.00

Total number of FTE Post Doctorates: 0.00

List of faculty supported by the grant that are National Academy Members

James E. McGrath

Names of Faculty Supported

James E. McGrath

Number of Faculty: 0.00

Names of Under Graduate students supported

Number of under graduate students: 0.00

Names of Personnel receiving masters degrees

Number of Masters Awarded: 0.00

Names of personnel receiving PhDs

Michael Hickner, Ph.D. Awarded December 2003, Current employer: Sandia National Laboratory, New Mexico  
Melinda Hill, Ph.D. anticipated May 2006

Number of PhDs awarded: 1.00

Names of other research staff

Sub Contractors (DD882)

Inventions (DD882)



The acronym BPSH has been developed to describe the multiphase copolymers that are derived from biphenyl sulfones in the acid form, where the xx rates to the mole fraction of the ion conducting hydrophilic moieties that are introduced. Thus, we will discuss in terms of BPSH 30-, 35-, 40, etc. During the past year a great deal of effort has been made to point out the differences between the pure hydrocarbon-based systems, and the partially fluorinated systems based upon fluorinated Bisphenol A. The overall reaction scheme to produce the copolymers is shown in Figure 2.

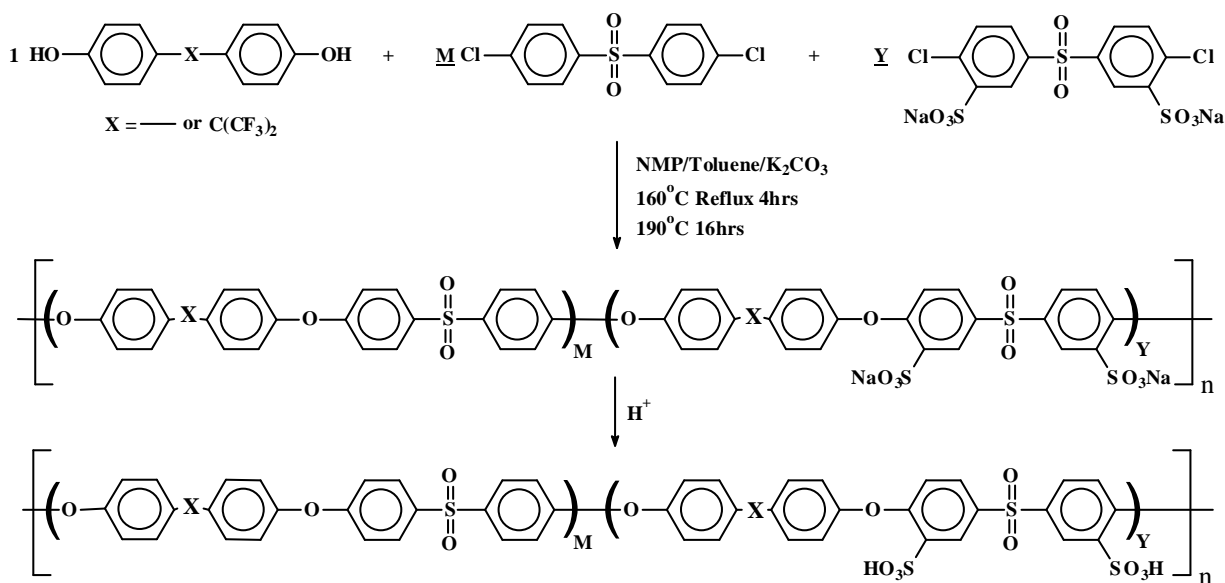


Figure 2. Synthesis of disulfonated poly(arylene ether sulfone) copolymers

The permeability of these materials, coupled with their drag capabilities are shown in Figure 3. Here the comparison between the 30, 35 and 40% copolymers with Nafion 117 is made. As one notes, the thin film conductivity decreases at room temperature as one decreases the concentration of ion conductors, as expected. However, very desirably, the methanol permeability in electro-osmotic drag also decreased quite significantly, allowing for improvements of more than 4 in the basic reduction of permeability to methanol and/or electro-osmotic drag in water. This is very important because the global or overall water uptake actually appears to be significantly higher.



	ion exchange capacity (meq/g)	water uptake (wt %)	conductivity (S/cm)	methanol permeability (cm <sup>2</sup> /s)	electro-osmotic drag coef. (N H <sub>2</sub> O/H <sup>+</sup> )
Nafion 117	0.91	19	0.11	16.7*10 <sup>-7</sup>	3.0
BPSH-40	1.71	58	0.10	8.1*10 <sup>-7</sup>	1.3
BPSH-35	1.51	38	0.08	5.6*10 <sup>-7</sup>	0.9
BPSH-30	1.32	31	0.06	3.6*10 <sup>-7</sup>	0.7

30°C in liquid water

Figure 3. Copolymer Characterization

As we have pointed out in a publication in *Macromolecules*, this is because the nature of the water is different in the aromatic sulfonic acid moieties, relative to Nafion. (Ref.: Y.S. Kim, L. Dong, M. Hickner, T.E. Glass, and J.E. McGrath, “State of Water of Disulfonated Poly(arylene ether sulfone) Copolymers and a Perfluoro Sulfonic Acid Copolymer (Nafion) and Its Effect on Physical and Electrochemical Properties,” *Macromolecules*, 36(17), 6281-6285 (2003). There is a higher component of strongly hydrogen-bonded and loosely hydrogen bonded systems and a lower component of “free water.” Thus, one can begin to develop models for how the transport system can be modeled and this is being pursued. The improved DMFC results can be correlated with the lower methanol permeability.

The composition and morphology control the methanol permeability in these membranes, as summarized below (Ref: Yu Seung Kim, Michael A. Hickner, Limin Dong, Bryan S. Pivovar, and James E. McGrath, “Sulfonated Poly(Arylene Ether Sulfone) Copolymer Proton Exchange Membranes: Composition and Morphology Effects on the Methanol Permeability,” *Journal of Membrane Science*, 243(1-2), 317-326, 2004).

Methanol permeability of directly copolymerized 4,4'-biphenol based disulfonated poly(arylene ether sulfone) copolymers (BPSH) was investigated with reference to utility as a proton exchange membrane (PEM) for direct methanol fuel cells (DMFC). Water uptake and dynamic mechanical analysis were coupled with previous observations that the PEM can have two functional morphological regimes, which depend on the degree of disulfonation (copolymer composition), acidification method, and hydrothermal treatment. The two regimes are observed by AFM to represent: (1) a “closed” structure where the hydrophilic copolymer chain segments essentially aggregate as isolated domains or (2) an “open” structure where the domain connectivity of the hydrophilic phase of the copolymers is achieved. It was demonstrated that methanol permeability (25°C) of the copolymers abruptly increased at copolymer compositions and processing conditions that influenced the membrane morphology to change from a closed to a much more open structure. The activation energy in the closed structure regime, ~20 kJ/mol-K,

was about 35 % higher than that in the open regime,  $\sim 15$  kJ/mol-K. The BPSH copolymers had higher selectivity than Nafion because of their remarkably lower methanol permeability, suggesting these materials hold promise for improved DMFC performance. Selectivity (e.g., proton conductivity/permeability) increased with the degree of disulfonation in closed structures, but decreased in the open structure regime. It is suggested that the optimum concentration of proton conducting groups for DMFC should be observed at or near the percolation threshold.

Indeed, performance comparison studies have been conducted by Drs. Y.S. Kim and B. Pivovar at Los Alamos National Labs on BPSH-30 in comparison with Nafion 112, which is a similar thickness, and even Nafion 1110, which is much thicker. The results, which are provided Figure 4, courtesy of our LANL colleagues, indicates significant improvement in both fuel efficiency and power density.

Nitrile containing copolymers have also been identified as excellent candidates for direct methanol fuel cells for proton exchange membranes. This is particularly true if the bisphenol is partly or completely derived from the hexafluorinated starting 6F bisphenol. Some of the results have recently been published and are summarized below (Ref: M.J. Summer, W.L. Harrison, R.M. Weyers, Y.S. Kim, J.E. McGrath, J.S. Riffle, A. Brink, M.H. Brink, "Novel Proton Conducting Sulfonated Poly(arylene ether) Copolymers Containing Aromatic Nitriles," *J. Membr. Sci.*, 239(2), (2004), 199-211).

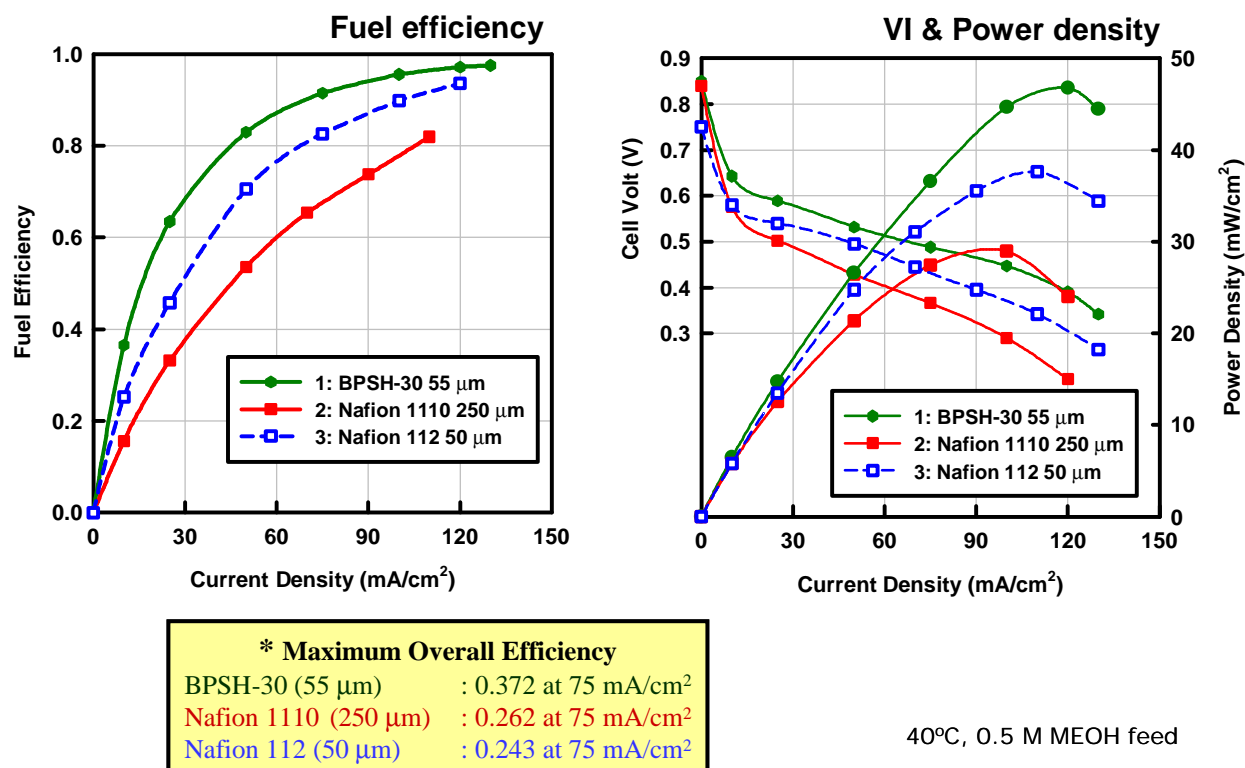
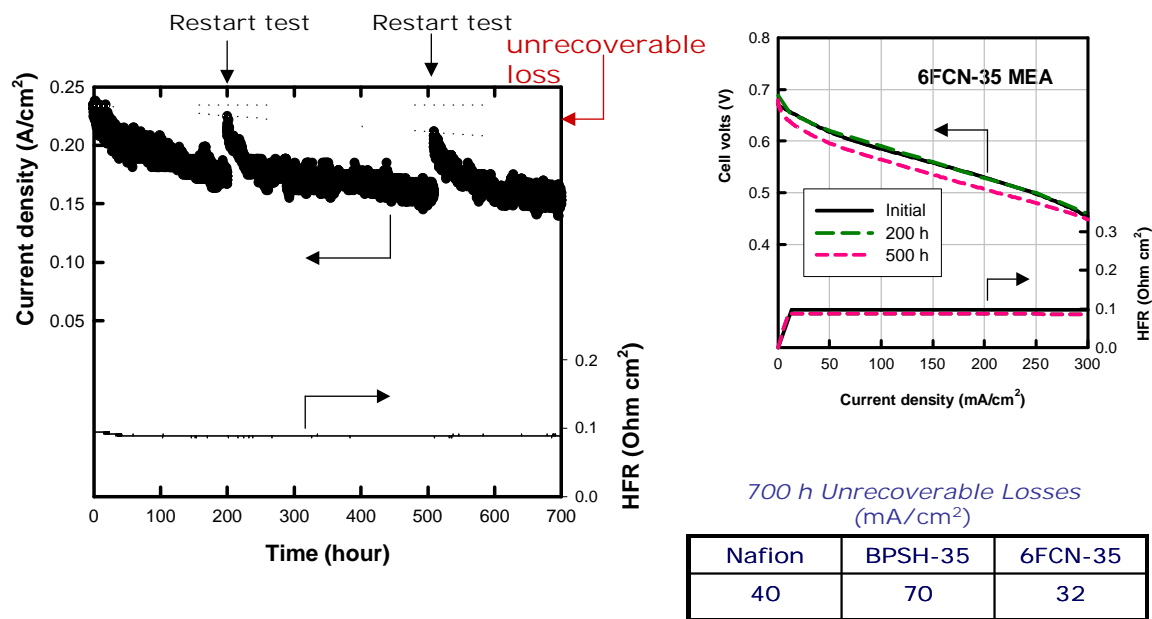


Figure 4. Performance Comparison – Cell Temperature

High mol. wt. nitrile-functional, (hexafluoroisopropylidene)diphenol-based poly(arylene ether) copolymers with pendent sulfonic acid groups were prepared by step copolymerization of 4,4'-(hexafluoroisopropylidene)diphenol, 2,6-dichlorobenzonitrile, and 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone. Copolymers containing as much as 55 mol% disulfonated units were cast from DMF solutions to form tough ductile films. The films were converted from the salt to the acid forms with dilute sulfuric acid followed by deionized water. Dynamic TGA demonstrated that the well dried, acidified, nitrile-containing copolymers had no wt. loss up to 300°C in air. A systematically varied compositional series showed increased glass transition temperatures, protonic conductivities, and hydrophilicities as a function of disulfonation. Films containing  $\geq 20$  mol% of the disulfonated repeat units had Tg's of 220°C and higher. At approximately equivalent ion exchange capacities (IEC), e.g. 1-1.6 meq g<sup>-1</sup>, the protonic conductivities of these films were comparable to other disulfonated poly(arylene ether sulfone) copolymers investigated. The benzonitrile-containing disulfonated copolymers also had reduced moisture absorption (10-15 wt.%) compared to other disulfonated poly(arylene ether sulfone) copolymers with equivalent IECs. The copolymer with 35 mol% of the disulfonated comonomer had a protonic conductivity of  $>0.10$  S cm<sup>-1</sup> at 110°C and 100% relative humidity. The protonic conductivities of the benzonitrile-containing copolymers decreased as expected as relative humidity was lowered. Atomic force microscopy in the tapping mode demonstrated that the acidified copolymer with 35 mol% disulfonated units was nanophase separated into an essentially co-continuous morphology of hydrophobic and hydrophilic domains. Further efforts are ongoing to translate these promising results into membrane electrode assemblies for proton exchange membrane fuel cell devices.

Initial life test results on the 6FCN35 were developed, again by Dr. Y.S. Kim at LANL, by preparing MEAs and measuring current density as a function of time at 80°C. The performance data expressed in terms of losses after 700 hours of aging, show that the nitrile sample is at least comparable to the Nafion control. This is also illustrated by the stability of the high frequency resistance (HFR) values over a 500 hour test period, as shown in Figure 5.



80°C, 0.5 M MEOH feed, 0.5 V cell potential

Figure 5. Life Test Result of 6FCN-35 MEA